# DEMONSTRATING NATURAL ATTENUATION WITH THE ELECTRIC POWER RESEARCH INSTITUTE'S MULTI-CHEMICAL GROUNDWATER TRANSPORT MODEL ROAM

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*REFERENCE: Proceedings of the 1999 Georgia Water Resources Conference,* held March 30-31, 1999, at the University of Georgia. Kathryn J. Hatcher, editor, Institute of Ecology, University of Georgia, Athens, Georgia.

**Abstract.** Natural attenuation recently became a widely accepted means of restoring groundwater resources. The Electric Power Research Institute's computer program called Remedial Options Assessment Model (ROAM) successfully predicted the outcome of natural attenuation for a complex mixture of dissolved coal tar and cyanide at a former manufactured gas plant site. The benefit of predicting natural attenuation with ROAM can be measured with monetary savings.

## INTRODUCTION

Natural attenuation is becoming a widely accepted means of restoring groundwater resources. Natural attenuation plans must include source removal and some form of proof that subsequent natural attenuation is a viable option for aquifer restoration. One means of showing natural attenuation success is to use groundwater transport models. This is a relatively simple task for sites with one or two contaminants. However, some sites, such as manufactured gas plants (MGPs), have multiple contaminants, which need to be abated. Conventional groundwater transport models are designed to simulate single-compound migration. Transport models designed to simulate complex, chemical mixtures are still new and not well understood.

The Electric Power Research Institute (EPRI) developed a computer program called Remedial Options Assessment Model (ROAM) for simulating groundwater transport of dissolved mixtures such as gasoline, diesel, and coal tar (Mills and others, 1993; Southern Company Services, 1997). ROAM was applied at a manufactured gas plant. The results show ROAM simulations can successfully predict the outcome of natural attenuation. The benefit of supporting natural attenuation with ROAM can be measured in monetary terms. Examples of industries, which can benefit from the use of ROAM include electric and gas utilities, wood preserving, petrochemical, and coking.

## BACKGROUND

Soil and groundwater contamination frequently occurs at petroleum facilities and historic manufactured gas plants. Remediation of these sites typically includes source removal and active groundwater treatment. The contaminants at these types of facilities include:

- Petroleum facilities -- gasoline, diesel, kerosene, and
- MGPs -- coal tar.

The common characteristic of these contaminants is that they are complex mixtures of monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs). Each individual compound in the mixture will behave differently in soil and groundwater settings depending upon its properties including:

- Solubility
- Vapor pressure
- Partitioning coefficient
- Diffusion rate, and
- Transformation rates for hydrolysis and biotransformation.

Each mixture is also very different because of the relative amounts and types of chemical present. Actual chemical partitioning in the soil and groundwater occurs according to Raoult's law (Mills and others, 1993). This law approximates the relative abundance of each chemical in a mixture and the phase of each

chemical. The different phases in a subsurface environment include:

- Separate phase liquids
- Vapor
- Dissolved, and
- Adsorbed

Most commercial grade contaminant transport models can predict phase relations for one compound. However, it is difficult to obtain justifiable initial conditions for any one chemical in a complex mixture because direct measurements will always make single compound models over-predict the amount of a chemical in the vapor, dissolved and adsorbed phases while the liquid phase may be under-estimated. This problem is compounded when the modeler has to predict the fate of more than one chemical. A case study will demonstrate ROAM's capability to simplify the task of multi-component transport while accurately predicting the fate of dissolved chemicals at an MGP site.

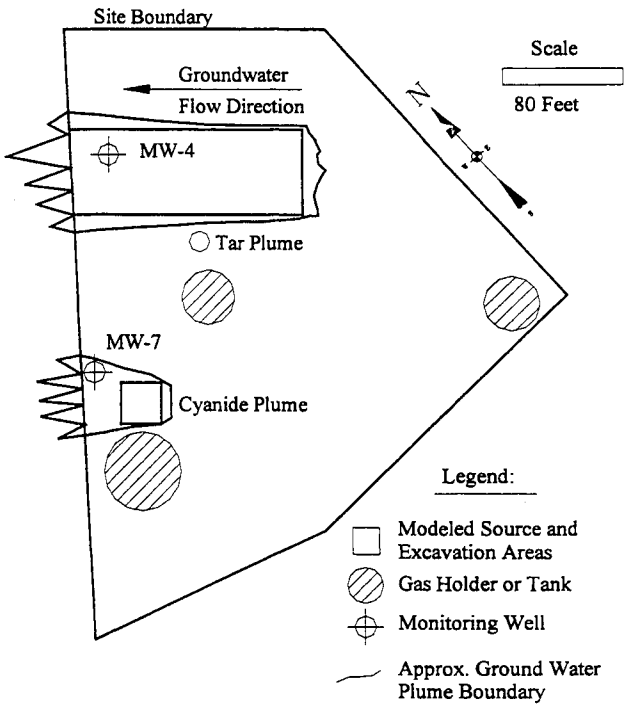


**Figure 1. Site layout showing groundwater plume boundaries.**

## FORMER MANUFACTURED GAS PLANT SIMULATION

A former MGP site located in the southeastern United States had coal tar and cyanide contaminated soils removed to reduce the potential for human exposure from contact, inhalation, and ingestion.
The site occupies approximately 2 acres in an area of light industry and a railroad switchyard. Figure 1 shows the site's water-table flow direction, and affected groundwater. The MGP tars are in a shallow and thin water-table aquifer. The aquifer is underlain by a 60-feet thick aquitard. The aquifer thickness ranges between 5 and 10 feet. Groundwater generally flows northwest at a rate of approximately 276 feet per year.

The actual source removal consisted of excavating approximately 13,000 cubic yards of coal tar and cyanide contaminated soils above and below the water table (Figure 2). Source removals, such as this, usually do not address groundwater issues. The source removal occurred in January 1998.

Future use of this site will be commercial or industrial, such that minor amounts of soil and groundwater contamination could be left for natural attenuation. Table 1 lists the highest observed concentrations and goals for the chemicals of interest.

ROAM has the ability to predict the transport and fate of complex mixtures of organic chemicals, such as coal tars or single chemicals. This simulation included a worst-case tar model and a cyanide model. The

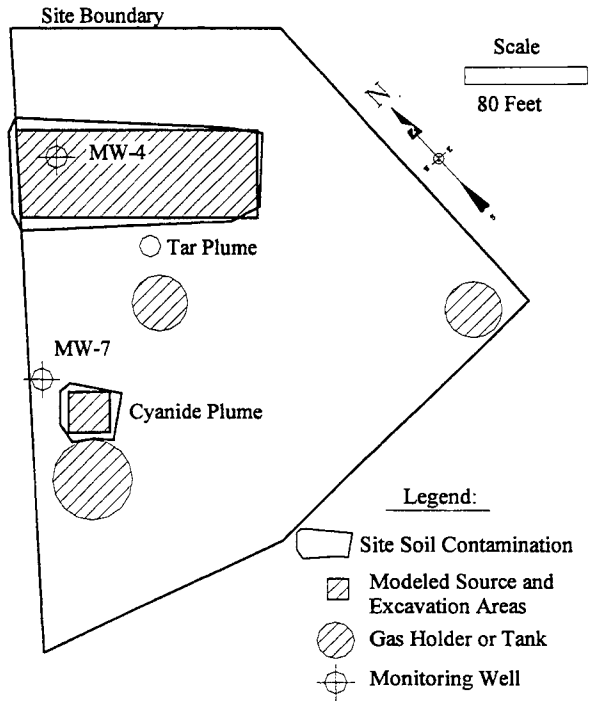


**Figure 2. Site layout showing site soil contamination and modeled source areas.**

**Table 1. Chemicals of Interest**

| Chemical | Highest Concentration (mg/l) | Concentration Goal (mg/l) |
|---|---|---|
| Benzene | 0.552 | 0.009 |
| Benzo(a)anthracene | 0.00428 | 0.00042 |
| Benzo(a)Pyrene | 0.00325 | 0.0002 |
| Naphthalene | 1.3 | 0.02 |
| Cyanide | 4.4 | 2 |

tar model used a built-in liquid-tar database, which contains all of the compounds typically monitored at MGP sites including PAHs, VOCs, and a substance called pitch. Pitch generally comprises from 50 to 80 percent of a coal tar. The model source area is a rectangular area, which is approximately 50 feet wide by 225 feet long with a thickness of 3.3 feet (Figure 2). All of the source tar was simulated within the saturated zone at the site. Since ROAM predicts transport for all chemicals in the coal-tar mixture, the model output was set up to list the fate of the four organic chemicals listed in Table 1.

The cyanide source area shown in Figure 2 is set in the upper few feet of the unsaturated zone and represents an area where gas purifier carbon was found. The source-area is approximately a 30 feet square area with a thickness of 1.5 feet. The source area concentration was set at 15,000 mg/kg. Most of the cyanide is made up of stable cyanide complexes such as ferrocyanides and ferricyanides (Prussian Blue and Prussian Green). The following site evidence suggested this assumption was appropriate for this site:

- Blue water in a monitoring well (which was located close to a deposit of purifier carbon).
- Relatively high total cyanide concentration as opposed to a lower, weak-acid disassociable cyanide concentration.

The total cyanide complex modeled had an approximate molecular weight of 215, an overestimated retardation factor of 68, and a high solubility. These characteristics assume worst-case transport conditions. The boundaries of the excavations are shown in Figure 2. Both excavations occurred simultaneously in reality and in the model. The timing of the tar and cyanide used the following chronology:

- Assumed initial release at the midpoint of the facility's operational life (1918).
- Source removal in 1998, which coincides with the actual source removal.
- Arbitrary ending date 20 years after source removal (2018).

## RESULTS

The chemicals simulated were benzene, benzo(a)pyrene, benzo(a)anthracene, naphthalene and cyanide. Typical pre-and post-remediation ROAM results for naphthalene are shown on Figure 3. Chemical-by-chemical results are described below:

- Benzene decreases after source removal and would meet the goal of 9 µg/l. Residual benzene was predicted to attenuate within 3 years and reach the practical quantification limit of 1 µg/l in less than 10 years.
- Benzo(a)pyrene was predicted to leach into groundwater, at levels between 1 and 6 µg/l in each of its tested scenarios. Pre-source removal results showed insignificant migration but persistent concentrations over time within the source area as a dissolved phase. ROAM predicted the excavation of the source tar would lower benzo(a)pyrene below its goal almost immediately. This may be attributable to its extremely low solubility in water.
- Benzo(a)anthracene was predicted to leach into groundwater, within the source area, at levels between 1 and 10 µg/l in the pre-remediation part of the simulation. Pre-source removal concentrations showed insignificant migration but persistence within the source area as a dissolved phase. The source removal indicated benzo(a)anthracene would meet a goal of 0.42 µg/l across the site. ROAM predicted less than one year would be necessary to achieve this goal. This may be attributable to its extremely low solubility in water.
- ROAM closely predicted the overall pattern for dissolved naphthalene for a 1996 sampling event (Figure 3). The other chemicals also coincided with measured analytical data. ROAM predicted naphthalene would achieve a reduction goal 20 µg/l in 2 to 10 years (worst case).
- Cyanide initially increased then asymptotically declined to a steady groundwater concentration in the pre-source removal portion. Source removal results showed cyanide would rapidly dissipate in

groundwater until the goal had been achieved in approximately 5 years.

In almost every case, ROAM over-predicted downgradient concentrations than were actually measured in the field. This circumstance is attributable to defining sorption characteristics in a transport model involving complex chemical mixtures.

After the source removal, several wells were re-analyzed for the chemicals of interest. Table 2 lists the predicted and actual concentrations as measure nearly 1 year after source removal. Table 3 lists the corresponding predicted versus actual times for achieving the site's natural attenuation goals.

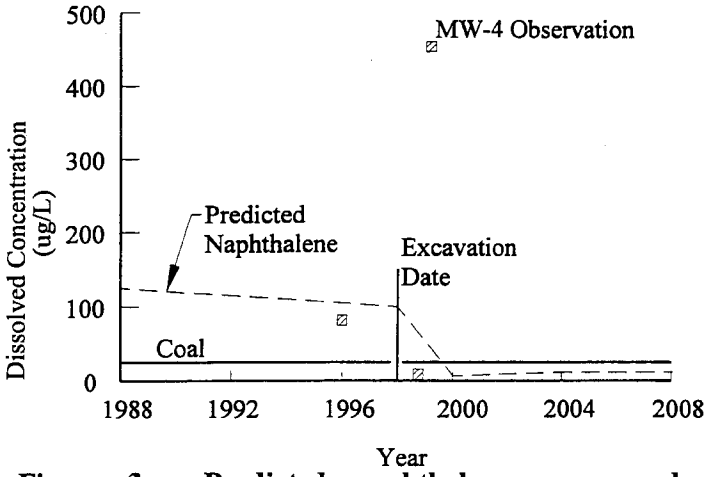


**Figure 3. Predicted naphthalene curve and observed concentration before and after source removal.**

## DISCUSSION

ROAM was used in several ways during this project. First, it allowed rapid decisions to be made, because it is a screening model used to see if any of the following actions are warranted:

- No further action.
- Active groundwater remediation.
- Natural attenuation.
- Determine if more work is necessary.

Secondly, the screening nature of the model makes it suitable for testing worst-case scenarios for supporting natural attenuation following source removals. At this site the ROAM results allowed a natural attenuation-monitoring program to be put in place instead of an active groundwater remediation system. This allows cost savings to be used to measure the value of using ROAM to demonstrate natural attenuation.

**Table 2. Predicted Versus Actual Concentrations and Reduction Times from the Source Area Wells.**

| Chemical | Well | Predicted Concentration | Measured Concentration |
|---|---|---|---|
| Benzene | MW-4 | <0.009 | 0.0019 |
| BaA | MW-4 | <0.001 | <0.001 |
| BaP | MW-4 | <0.001 | <0.001 |
| Naphth | MW-4 | 0.084 | 0.0813 |
| Cyanide | MW-7 | 0.1 | <0.001 |

BaA = Benzo(a)anthracene
BaP = Benzo(a)pyrene
Naphth = Naphthalene
Concentrations listed in mg/l

**Table 3. Predicted Versus Actual Reduction Times from the Source Area Wells.**

| Chemical | Well | Predicted Reduction | Measured Reduction |
|---|---|---|---|
| Benzene | MW-4 | <3 | <1 |
| BaA | MW-4 | <1 | <1 |
| BaP | MW-4 | <1 | <1 |
| Naphth | MW-4 | <1 | 93%within 1 year |
| Cyanide | MW-7 | <5 | <1 |

BaA = Benzo(a)anthracene.
BaP = Benzo(a)pyrene.
Naphth = Naphthalene.
Times listed in years.

Considering the contamination plumes shown in Figure 2, it is evident that there are two separate plumes, one of dissolved cyanide and the other of mixed MAHs and PAHs. Groundwater treatment equipment was estimated to be $300,000 for the cyanide plume and MAH and PAH plume. Engineering, operations and maintenance are estimated to be $125,000 per year for up to 7 years. This results in a total, estimated savings of $1,175,000. This

amount would be required on top of the required source removal cost.

Lastly, it should be noted that five chemicals were simulated. ROAM's ability to simulate all source areas simultaneously greatly reduced the amount of time necessary to model various remedial scenarios. This part of the overall cost is low compared to the savings realized during remediation. Over all time spent in ROAM execution and testing was less than two weeks.

## CONCLUSIONS

ROAM was used to enhance understanding of natural attenuation's role in remediating a site for MAHs, PAHs, and cyanide. Results show rapid dissipation in the former source areas for low solubility chemicals and up to seven years for higher solubility chemicals. Actual groundwater improvements occurred in a shorter time period than the worst-case scenario simulations predicted. ROAM's ease-of-use enabled this project to proceed at an accelerated pace in order to make time decisions which ultimately saved money.

## ACKNOWLEDGEMENTS

The author would like to thank David Morris and Jim Redwine for their support and review of this paper. The author would also like to thank April Cole for her assistance in preparing the manuscript for publication.

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